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A 3D luminescent Zn(II) coordination polymer with rutile-type topology

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ABSTRACT

A new coordination network, namely $\{[Zn(bce)(H_2O)]\}_n$ (**1**) (H_2bce = 1,2-bis(4-carboxy-phenoxy)ethane), is reported. Complex **1** shows a 3D (3,6)-connected rutile (**rtl**) topology. The luminescence study indicates that the title compound emits bright green fluorescence and possesses moderate fluorescence lifetimes ($\tau = 2.26$ ns).

The rational design and construction of metal-organic frameworks (MOFs) from metal ions and flexible organic ligands have been receiving increasing interest for fascinating structural topologies, interesting conformations such as pillared-layer structure, and potential applications [1]. Until recently, research on coordination polymers has focused on incorporation of flexible dicarboxylate ligands due to its flexuous geometry and various binding modes [2–8]. Inspired by our previous experience, we have been interested in the syntheses and characterizations of different polymers containing 1,3-bis(4-carboxy-phenoxy)propane (H_2bcp) and 4,4′-oxybis(benzoic acid) (H_2oba) [9–12]. Between the two types of flexible dicarboxylate ligands, the segments of $-O-(X)_n-O-$ chains are different with the relative orientation of CH_2 groups ($X = CH_2$; $n = 0$ for H_2oba; and $n = 3$ for H_2bcp). Herein, we explore a similar flexible dicarboxylate ligand 1,2-bis(4-carboxy-phenoxy)ethane (bce) to construct new type of motifs and infer the relationship between the feature of functions and structural characters.

Herein, we report the synthesis and characterization of a new 3D coordination polymer, in which bce ligands work as pillars and link the inorganic $-Zn-CO_2-Zn-$ layers, resulting in (3,6)-connected rutile-type framework. The as-synthesized sample of compound **1** has also been measured by IR, PXRD, elemental, TG analyses and 3D luminescence.

Colorless crystals of compound **1** were thermally synthesized by reacting $Zn(OAC)_2 \cdot 4H_2O$ and H_2bce in molar ratio 1:1 and mixed methanol/deionised water solvent at 150 °C for 72 h [13].

The structure of **1** contains one unique Zn atom, one unique bce, and one coordinated water molecule. Fig. 1a shows the stick view of the local octahedral-coordination geometry around the Zn(II) atom. The axial positions are occupied by two oxygen atoms from different carboxyl groups, whereas the three oxygen atoms from carboxyl groups in bridging bidentated $[(k^1–k^1)\text{-}\mu_2]$ and tridentated $[(k^2–k^1)\text{-}\mu_3]$ fashions and one oxygen atom from coordinated water molecule are on the equatorial plane. Thus, each Zn(II) ion is coordinated by five carboxylate oxygen atoms from three different bce ligands, in which is similar with the reported complexes with oba [14]. The bond distances of Zn–O are in the range of 2.152(5) to 2.361(5) Å and the O–Zn–O bond angles vary from 55.59(18) to 168.1(2)°, which is coincident with the reported values of the corresponding Zn–carboxylate compounds. Carboxylate groups link the Zn(II) center to form 2D sheets which runs parallel *bc*-plane (Fig. 2b). The 2D layer consists of dimmers of edge sharing ZnO6 polyhedron that are corner-shared hexagon to form the layer. The distance between the Zn(II) atoms in each dimmer is 3.72(12) Å, while the distance between the Zn atoms of corner-shared interaction is 4.87(11) Å. Each bce ligand links to three Zn(II) atoms in bridging bidentated $[(k^1–k^1)\text{-}\mu_2]$ and tridentated $[(k^2–k^1)\text{-}\mu_3]$ modes. To the best of our knowledge, this type of coordinating mode of bce ligand is not observed in the previously reported complexes. The usual mode is bridging bidentated $[(k^1–k^1)\text{-}\mu_2]$ and monodentated $[(k^1)\text{-}\mu]$ modes for carboxyl groups. The layers are separated by the biphenyl dicarboxylate groups with the biphenyl rings layered along the *ab*-plane. The flexible bce ligands along the *a* axis act as a pillar and serve to connect adjacent layer to shape an extended 3D coordination motif, as shown in Fig. 2a. Unfortunately, the adjacent pillars are too close to each other, and there is no solvent accessible void in **1**.

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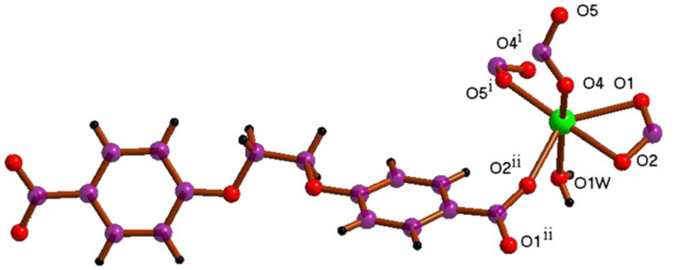

Fig. 1. The coordination geometry of the metal center and the ligand geometry of compound **1**. (Symmetric codes: (i) x, −y + 1/2, z + 1/2; (ii) −x + 1, −y + 1, −z + 1.)

A better insight into the nature of **1** can be achieved by the application of topological approach, reducing multidimensional structures to simple node-and-linker nets. As discussed above, the dinuclear Zn subunits can be regarded as one node. Each subunit is surrounded by six adjacent bce ligands, thus, each subunit is taken as a six-connected node. On the other hand, each bce ligand can be considered as a three-connecting node since it links three subunits. Consequently, according to the calculation of TOPOS [15], the framework of **1** belongs to a uninodal (3,6)-connected **rtl** type of topology with Schläli symbol of $(4\cdot6^2)_2(4^2\cdot6^{10}\cdot8^3)$ (Fig. 3) [16]. This is a new topological motif in the MOFs with bce ligand.

As to FTIR spectra, the compound shows a broad band center around 3437 cm^{-1} attributable to the O–H stretching frequency of the water molecule in **1**. As shown in Fig. S1. To study the stability of the polymer, thermogravimetric analysis (TGA) of complex **1** was performed (Fig. S2). The compound **1** has two observed weight loss, first weight loss of 4.6% is corresponding to the loss of the crystallization water (calcd 4.7%). Additionally, to confirm the phase purity of compound, the original sample was characterized by X-ray powder diffraction (XRPD) at room temperature. The pattern that was simulated from the single-crystal X-ray data of compound was in agreement with those that was observed, as shown in Fig. S3. For compound **1** after heating at 190 °C for 5 h, the coordinated water molecule was removed (the evacuated framework is defined as **1**′). The XRPD pattern of **1**′ is similar to compound **1**, although minor differences can be seen in the positions, intensities, and widths of some peaks, which indicates that the framework of compound **1** is retained after the removal of the water molecule.

Organic–inorganic coordination polymers, especially those with d^{10} metal centers, have been investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as light-emitting diodes (LEDs) [17]. Therefore, the complex **1** and bce were studied in the solid-state at room temperature. Excitation of the microcrystalline sample at 266 nm leads to the generation of fluorescent emission, with the peak maxima occurring at 364 nm for **1**, as shown in Fig. 4a. To further understand the origin of these emission bands, the fluorescent spectrum of bce ligand has been also measured, which shows a relatively broad band at 348 nm ($\lambda_{ex} = 260$ nm) (Fig. 4b). The emission bands of these carboxylates can be assigned to the $p^* \to n$ transition as previously reported. The luminescence decay curve of **1** was obtained at room temperature. The decay curves are well fitted into an exponential function. As shown in Fig. S4. The corresponding lifetime for **1** is about $\tau =$ 2.26 ns at 364 nm. The χ^2 value is found to be close to 1 in this work. Deng and his co-worker reported a Zn(beta) complex and its lifetime ($\tau = 13.81$ ns), which is longer than that of **1**. The difference may be attributed to the 3D connection feature and more rigid frameworks between complexes Zn(beta) and title compound **1**, in which also results in less vibrations of the skeleton and less radiation decay of energy [18].

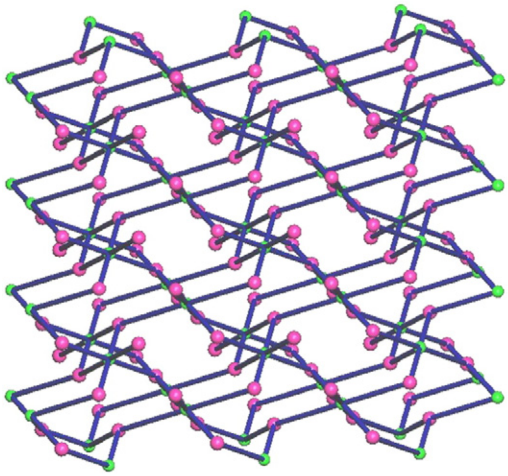

Fig. 3. Schematic representation of the 3D **rtl** topology net of **1**.

In conclusion, a new Zn(II) coordination polymer of $\{[Zn(bce)(H_2O)]\}_n$, has been successfully synthesized, in which shows a 3D (3,6)-connected rutile (**rtl**) topological motif. In addition, the luminescence behavior and lifetime of **1** at room temperature are discussed.

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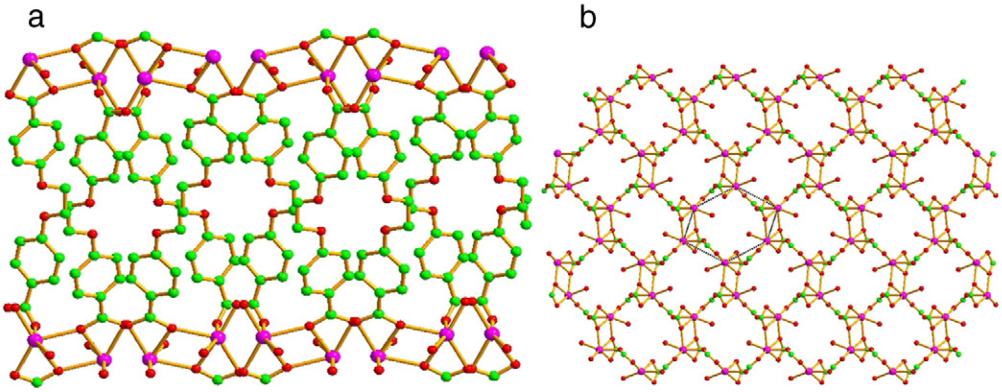

Fig. 2. (a) View of the 3D pillared-layer network along the *a*-axis for **1**; (b) the 2D layer of **1** with Zn bridged by oxygen atoms from the carboxylate groups of bce ligands.

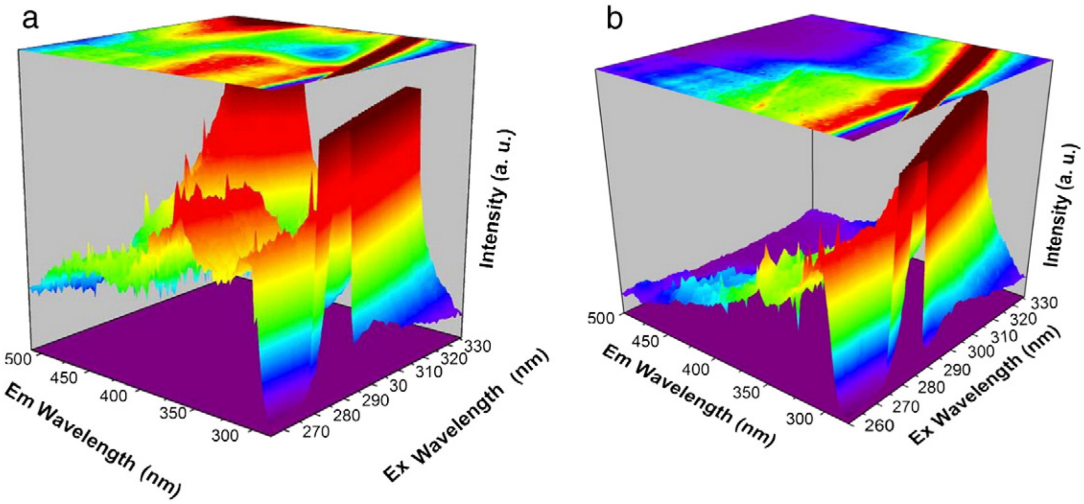

Fig. 4. (a) View of the 3-D fluorescence spectrum of **1** and (b) the 3-D fluorescence spectrum of bce ligand at room temperature.

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Appendix A. Supplementary material

Supplementary data(including four figures and supplementary crystallographic data in CIF for this paper) to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.03.010.

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[13] A mixture of $Zn(OAC)_2 \cdot 4H_2O$ (0.027 g, 0.1 mmol), H_2bce (0.023 g, 0.1 mmol), CH_3OH (5 mL) and deionised water (10 mL) was stirred for 30 min in air. The pH of the resulting solution was adjusted to 7 using dilute NaOH (0.1 mol/L) and kept at 150 °C for 72 h. The solution was then cooled to room temperature at rate of 5 $°C\ h^{-1}$, to colorless crystalline product **1** in 41% yield based on Zn. $C_{16}H_{14}ZnO_7$ (383.64). Calcd: C, 50.08; H, 3.68; Found C, 50.16; H, 3.882. IR (KBr, cm^{-1}): 3437(vs); 2968(m), 1605(s), 1506(s), 1402(vs), 1251(s), 1164(s), 1054(m), 857(s), 781(m), 659(m). Crystal data for **1**: $C_{16}H_{14}ZnO_7$, $M_r = 383.64$, monoclinic, space group $P2_1/c$, $a = 15.840(6)$ Å, $b = 11.339(5)$ Å, $c = 8.643(4)$ Å, $\beta = 98.688(6)°$, $V = 1534.6(11)$ Å^3, $Z = 4$, $D_{calcd.} = 1.661\ g/cm^3$, $\mu = 1.637\ mm^{-1}$, $R_1[2\sigma(I)] = 0.0666$, wR_2(for all data) = 0.1703. **CCDC**: 915140.

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